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(54) **TITLE OF THE INVENTION:**

Dielectric thin film and a method for forming the thin film

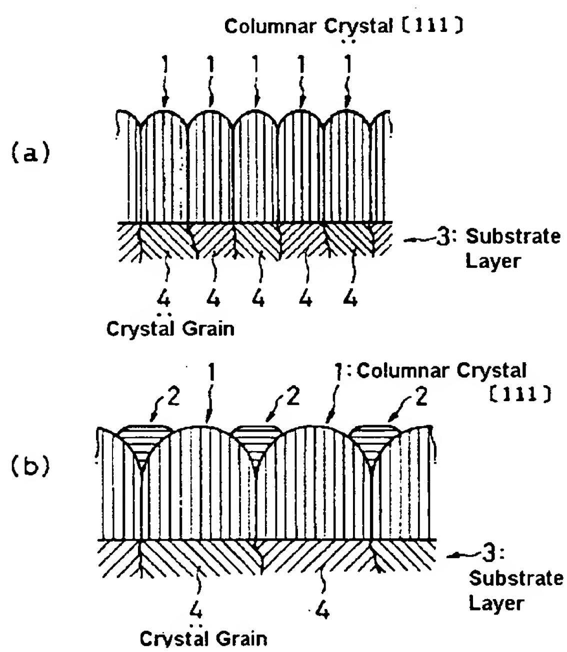
(57) **ABSTRACT**

PROBLEM TO BE SOLVED:

To increase the residual polarization value of a lead zirconate titanate (PZT) dielectric thin film formed on a Pt substrate layer.

SOLUTION:

With a PZT dielectric thin film formed on a Pt substrate layer 3, the crystal grain diameter of the Pt substrate layer is kept down to 50 nm or less.



SPECIFICATION

CLAIMS

What is claimed is:

1. A dielectric thin film comprising a lead zirconate titanate (PZT) dielectric thin film formed on a Pt substrate layer, wherein the crystal grain diameter of the Pt substrate layer is 50 nm or less.

2. A dielectric thin film according to claim 1, wherein the residual polarization value of the dielectric thin film is 50 $\mu C/cm^2$ or higher.

3. A dielectric thin film according to claim 1, wherein the Pt substrate layer is comprised of a Pt or Pt-Ti alloy layer.

4. A method for forming a dielectric thin film used to form a PZT dielectric thin film on a Pt substrate layer, wherein the crystal grain diameter of the Pt substrate layer is 50 nm or less.

DETAILED DESCRIPTION OF THE INVENTION

[0001]
Technical Field of the Invention

The present invention relates to the PZT dielectric substance and a method for forming the dielectric substance. Specifically, the present invention relates to dielectric substances having high residual polarization values and to a method for forming the dielectric substance.

[0002]
Description of the Related Art

The applications of ferroelectric substance in the electronics field are varied, including pyroelectric infrared sensors, piezoelectric elements, electro-optic elements, memory elements, and capacitors. With the miniaturization and integration of electronic components brought about by advances in semiconductor technology in recent years, progress is being made in miniaturizing ferroelectric elements and reducing the film thickness. In addition to having a high dielectric constant, PZT ($PbZr_{1-x}Ti_xO_3$, $0 \leq x \leq 1$) has a high spontaneous polarization and a high Curie temperature, as well as large piezoelectric and electro-optic effects. Moreover, it has low coercive field, and its polarization can be reversed readily.

[0003]
With regard to thin-film condensers that are formed on Si boards, some have a lower electrode, a dielectric thin film and an upper electrode laminated onto the board in that order, while others use the board as the lower electrode and have a dielectric thin film and an upper electrode

laminated directly thereon, in that order.

[0004]
When PZT is used as a material to make capacitors for Si semiconductor memories, a lower electrode is generally formed. In this instance, however, no reaction with oxygen takes place at the lower electrode: Pt or Pt-Ti alloy is generally used for a number of reasons, one being that the lattice constant is close to that of the perovskite structure of PZT.

[0005]
Moreover, during the process of manufacturing a device, the substrate is formed on the SiO_2 layer on the surface of the Si board. For this reason, a Ti layer is usually formed in between the Pt layer and the Si board for various reasons, such as to improve the adhesion of Pt and SiO_2 and to control the diffusion of Pb into the SiO_2 layer.

[0006]
The deposition of the Pt, Pt-Ti, and Ti layers is generally performed by vapor deposition or sputtering. The sol-gel method, sputtering and the metal organic chemical vapor deposition (MOCVD) method and the like are used to form a film of PZT or lanthanum-modified lead zirconate titanate (PLZT).

[0007]
Problems to be Solved by the Invention

The inventors of the present invention conducted various research on the PZT ferroelectric thin film. As a result, it was found that the crystal grain diameter of the substrate layer that were made of Pt or a Pt-Ti alloy has a considerable effect on the residual polarization value.

[0008]
The aim of the present invention is to raise the residual polarization value of a PZT dielectric thin film formed on a Pt substrate layer.

[0009]
Means for Solving the Problems

The dielectric thin film of the present invention is comprised of a PZT dielectric film formed on a Pt substrate layer, and the crystal grain diameter of the Pt substrate layer is 50 nm or less.

[0010]
The method for forming dielectric thin film according to the present invention uses a method of forming PZT dielectric thin film on a Pt substrate layer, wherein the crystal grain diameter of the Pt substrate layer is kept to 50 nm or less.

[0011]
Keeping the crystal grain diameter of the substrate layer to 50 nm or less in this manner normally

causes a conspicuous rise in the residual polarization value of the PZT, to a level of 50 $\mu C/cm^2$ or higher.

[0012]
The ideal substance for use as the substrate layer is Pt or a Pt-Ti alloy.

[0013]
Description of the Preferred Embodiments

The ideal board to form the substrate layer of the present invention is an Si board. An SiO_2 layer is formed on the surface of the Si board by thermal oxidation, preferably to a thickness in the range of 100 to 1,000 nm. As for the substrate layer, which is formed on the board, Pt or a Pt-Ti alloy, whose respective grid constant approximates that of PZT, is used.

[0014]
It is desirable that the Ti content of the Pt-Ti alloy be 4 wt % or less, preferably from 2 to 5 wt. % [sic].

[0015]
It is desirable that the thickness of the substrate layer be 100 to 300 nm, preferably 150 to 200 nm. It is preferable that the substrate layer be formed by sputtering or by electron-beam vapor deposition. During the sputtering or electron-beam vapor deposition, the crystal grain diameter of the substrate layer formed can be kept to 50 nm or less by controlling the temperature and the deposition rate. It is especially preferable that the crystal grain diameter be 10 to 45 nm.

[0016]
The optimum conditions for the sputtering are a temperature of 200°C or less and a deposition rate of 200 Å/min, preferably 20 to 100°C and 50 to 200 Å/min, respectively. Using these conditions ensures that the crystal grain diameter of the substrate layer can be kept to 50 nm or less. Moreover, performing electron-beam vapor deposition at a temperature of 200°C or less makes it possible to obtain a crystal grain diameter of 50 nm or less for the substrate layer.

[0017]
Incidentally, it is desirable that a Ti layer of 10 to 50 nm, preferably 10 to 30 nm, be formed between the substrate layer and the Si board in order to improve the adhesion of the substrate layer to the board and to prevent the diffusion of Pb.

[0018]
It is desirable that the thickness of the PZT dielectric thin film formed on the substrate layer be 100 to 400 nm, preferably 100 to 300 nm. The PZT film can be formed using methods such as the sol-gel, sputtering, or chemical vapor deposition (CVD) method. The general expression for the PZT of the PZT dielectric thin film is $PbZr_{1-x}Ti_xO_3$, $(0 \leq x \leq 1)$. However, it is preferable that x be $0.2<x<0.8$.

[0019]
The PZT dielectric thin film may be comprised of only PZT, or it may also contain 15 mole percent or less of substances such as La.

[0020]
In the present invention, keeping the crystal grain diameter of the substrate layer to 50 nm or less caused the residual polarization value to increase. The reason for this is surmised as described below.

[0021]
The Pt or Pt-Ti alloy, which is on the surface of the substrate layer serving as the lower electrode, is oriented roughly in the direction of [111] under all conditions under which the deposition is performed. The perovskite crystal structure of the PZT grows in a columnar form according to the diameter and the orientation of a crystal grain 4 of the Pt or Pt-Ti of the board comprising a substrate layer 3. If the crystal grain diameter is too large, then columnar crystals 1 of the PZT also become too large, as shown in FIG. 1(b), and this causes the growth of crystal grains 2, which are oriented in a direction different from [111], in-between columnar crystals 1, which are too large. As more crystal grains 2, which are not oriented in the direction [111], are formed, the residual polarization value decreases.

[0022]
When the crystal grain diameter of the substrate layer 3 becomes 50 nm or less, this causes the columnar crystals 1 to become smaller, as shown in FIG. 1(a), so that virtually no crystal grains with a different orientation are formed in-between columnar crystals 1. In other words, virtually all columnar crystals are oriented in the direction of [111], thereby raising the residual polarization value.

[0023]
Examples

Examples 1 and 2; comparative examples 1 and 2

Examples and comparative examples, wherein a Pt layer is formed as a substrate layer, will be described first.

[0024]
An SiO_2 layer of a thickness in the range of 600 nm was formed by thermal oxidation performed on the surface of an Si (100) wafer.

[0025]
Next, a 30-nm Ti thin film was formed on the board thus obtained by means of a DC sputter with the deposition rate set at 179 Å/min, using Ar at 30 sccm and 800 W, with the board at room temperature. Then, a Pt thin film having a thickness of 200 nm was formed with the deposition

rate set at 290 Å/min, using Ar at 30 sccm and 500 W, with the temperature of the board at 450°C (comparative example 1), 300°C (comparative example 2) and at room temperature (example 1). In the case of example 2, electron-beam vapor deposition was used in place of the DC sputter to form a Ti thin film (at a deposition rate of 50 Å/min) and a Pt thin film (at a deposition rate of 20 Å/min) to form the same respective thickness as those described above.

[0026]
The crystal grain diameter of each Pt film was found to be as shown in TABLE 1. Moreover, the crystal grain diameter was measured in the usual manner. The deposition surface was observed by means of a scanning electron microscope in order to measure the grain diameter, and the mean value was then obtained.

[0027]
The PZT thin film was prepared on the surface of the Pt substrate layer by the sol-gel method. In the first place, in order to prevent the formation of rosettes on the surface of the PZT thin film due to a deficiency of Pb, a coating of 1% $PbTiO_3$ solution was applied on the surface by spin-coating under the following conditions: 3 seconds at 500 rpm/min and 15 seconds at 3,000 rpm/min, followed by baking under the conditions of 400°C for 10 minutes. It was then coated with a 10% PZT solution (110:52:48) in a similar manner for 3 seconds at 500 rpm/min and for 15 seconds at 3,000 rpm/min, dried for 5 minutes, and then pre-baked for 10 minutes at 400°C. After this process was repeated five times, it was subjected to baking at 600°C for 60 minutes to crystalize the PZT. In this manner a PZT thin film having a thickness of 200 nm was obtained.

[0028]
An upper electrode was then prepared by the vacuum vapor deposition method using gold, and D-E hysteresis was determined. The residual polarization values obtained from the D-E hysteresis are shown in TABLE 1.

[0029]
Examples 3 and 4; and comparative examples 3 and 4.

Examples and comparative examples in which a layer of a Pt-Ti alloy (96 wt % Pt : 4 wt % Ti) as the substrate layer will be described next.

[0030]
An SiO_2 layer, Ti thin film, and a Pt-Ti alloy thin film were formed respectively using the method for forming an SiO_2 layer and the deposition method used to coat it according to examples 1 and 2 and comparative examples 1 and 2 (however, the deposition rate for the Pt-Ti alloy thin film was changed to 130 Å/min).

[0031]
The upper electrode was then formed in a similar manner to the one described above, and the

residual polarization value was measured. The results of the determination are shown in TABLE 1, along with the crystal grain diameter of the substrate layer.

[0032]

TABLE 1

Substrate Layer (SL)	Pt				Pt-Ti			
Conditions for SL Formation	Sputter 450°C	Sputter 300°C	Sputter room temp.	Electron-beam vapor deposition: room temp.	Sputter 450°C	Sputter 300°C	Sputter room temp.	Electron-beam vapor deposition: room temp.
Mean Crystal Grain Diameter (nm) of SL	123	75	41	20	150	69	38	25
Residual Polarization Value ($\mu C/cm^2$)	39.9	41.1	52.8	55.3	36.5	40.8	56.1	55.4

[0033]
As shown in TABLE 1, it is clear that keeping the crystal grain diameter to 50 nm or less causes a conspicuous rise in the residual polarization value.

[0034]
Advantages of the Invention

As described above, the present invention provides dielectric thin membranes having conspicuously high residual polarization values. Moreover, it is conceivable that ferroelectric thin membrane memories will become even more highly integrated in the future. However, if the residual polarization were to cause a reduction in the electricity storage capacity of capacitor components having ferroelectric materials, then this would cause a rise in the soft error rate due to alpha rays, thus making it useless.*

* The use of the ferroelectric thin film prepared according to the present invention offers excellent advantages in that it checks the reduction in the electricity storage capacity, thus preventing soft errors.

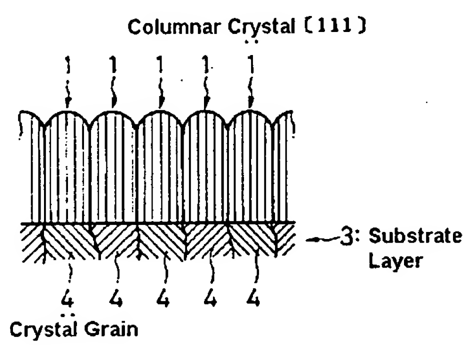
Brief Description of the Drawings

FIG. 1 is a schematic cross-sectional view of columnar crystals growing on the substrate layer.

Description of the Reference Numerals

1. Columnar crystal (oriented in the direction of [111]
3. Substrate layer

(a)



(b)